IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of	)	
	)	
Gino PALUMBO, et al.	)	Group Art Unit: 1795
	)	
Patent Application No.: 10/516,300	)	Examiner: W. T. Leader
	)	
Filed: December 9, 2004	)	Confirmation No.: 5590
	)	
For: PROCESS FOR ELECTROPLATING METALLIC AND METALL MATRIX COMPOSITE FOILS, COATINGS AND MICROCOMPONENTS	)	Attorney Dkt No.: BROO3001/ESS

APPEAL BRIEF PURSUANT TO 37 C.F.R. 41.37

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

A Notice of Appeal and a Pre-Appeal Brief Request for Review were filed in the U.S.P.T.O electronically on 22 January 2010. A Decision on the Pre-Appeal Brief Request directing proceeding to the Board of Appeals and Interferences was mailed on March 24, 2010.

Compliance with 37 C.F.R. 41.37 follows:

37 C.F.R. 41.37(c)(1)(i)

Real Party in Interest

The real party in interest is Integran Technologies, Inc.

37 C.F.R. 41.37(c)(1)(ii)
Related Appeals and Interferences

There are no related appeals and interferences.

37 C.F.R. 41.37(c)(1)(iii)
Status of Claims

Claims 1-8 and 10-34 are finally rejected and are the appealed claims.

Claims 9 have been canceled.

37 C.F.R. 41.37(c)(1)(iv)
Status of Amendments Subsequent to Final Action

There were no amendments subsequent to final action.

37 C.F.R. 41.37(c)(1)(v)
Summary of the Claimed Invention for
Each Independent Claim Involved in the Appeal

There are three independent claims involved in the appeal, namely claims 1, 31 and 33.

All the claims are directed to a per cathode or per anode area agitation rate as a process variable in depositing nanocrystalline metallic material, i.e. agitation rate normalized to electrode area as a process variable in depositing nanocrystalline metallic material. Nanocrystalline metallic materials is defined as having microstructure with an average grain size less than 100 nm. (See next page)

Claim 1 is directed to cathodically electrodepositing (application as filed at page 14, lines 17-25) a selected metallic material (application as filed at page 5, line 9) on a

permanent or temporary substrate (application as filed at page 6, line 16) in nanocrystalline form (application as filed at page 6, line 9) with an average grain size less than 100 nm (application as filed at page 11, line 7) by electrodeposition (application as filed at page 1, line 13) at a deposition rate of at least 0.05 mm/h (application as filed at page 6, line 3) comprising providing an aqueous electrolyte (application as filed at claim 1) containing ions of said metallic material (application as filed at claim 1) and agitating the electrolyte at a per anode or cathode area agitation rate of 0.0001 to 10 liters per minute per cm^2 anode or cathode area (application as filed at page 5, lines 20-21).

Claims 31 is directed to a process for cathodically electrodepositing (application as filed at page 4, lines 17-25) a selected metallic material (application as filed at page 5, line 9) on a permanent or temporary substrate (application as filed at page 6, line 16) in nanocrystalline form (application as filed page 6, line 9) with an average grain size less than 100 nm (application as filed at page 11, line 7) at a deposition rate of at least 0.05 mm/h (application as filed at page 6, line 3) comprising providing an aqueous electrolyte (application as filed at claim 1) containing ions of said metallic material (application as filed at claim 1), agitating the electrolyte at a per anode or per cathode agitation rate of 0.0001 to 10 liters per minute per cm^2 anode or cathode area (application as filed at page 5, lines 20-21), and passing single or multiple cathode-current pulses between said anode and said cathode (application as filed at claim 1)

Claim 33 is directed to a process for cathodically electrodepositing (application as filed at page 1, lines 17-25) a selected metallic material (application as filed at page 5,

line 9) on a permanent or temporary substrate (application as filed at page 6, line 16) in nanocrystalline form (application as filed at page 6, line 9) with an average grain size less than 100 nm (application as filed at page 11, line 7) at a deposition rate of at least 0.05mm/h (application as filed at page 6, line 3) comprising providing an aqueous electrolyte (application as filed at claim 1) containing ions of said metallic material (application as filed at claim 1) and agitating the electrolyte at a per anode or cathode agitation rate in the range of 0.0001 to 10 liters per minute per cm^2 anode on cathode area (application as field at page 5, lines 20-21)

37 C.F.R. 41.37(c)(1)(vi)

Grounds of the Rejection to be Reviewed on Appeal

There are four grounds of rejection as follows:

1. Whether claims 1-8, 10-12, 15, 17, 27-31 and 33 are unpatentable under 35 U.S.C 103(a) over Erb et al. (US 5,433,797) in view of Lowenheim and additionally in view of Biberbach et al. (US 3,929, 595) and Gonzalez et al. (6,743,346).

2. Whether claims 16, 18-25 and 32 are unpatentable under 35 U.S.C 103 (a) as being unpatentable over Erb et al. in view of Lowenheim, Biberbach et al. and Gonzalez et al. as applied to claims 1-8, 10-12, 15, 17, 27-31 and 33 further in view of admitted prior art.

3. Whether claims 13 and 14 are unpatentable under 35 U.S.C. 103 (a) as being unpatentable over Erb et al. in view of Lowenheim additionally in view of Biberbach et al. and Gonzalez et al. as applied to claims 1-8, 10-12, 15, 17, 27-31 and 33 further in view of Uzoh et al (US 7,378,004).

4. Whether claim 26 is unpatentable under 35 U.S.C 103 (a) as being unpatentable over Erb et al. in view of Lowenheim in view of Biberbach et al., Gonzalez et al. and admitted prior art as applied to claims 16, 18-25 and 32 further in view of Hutkin (US 4,088,544).

Reconsideration of all the rejections is requested .

37 C.F.R. 41.37(c)(1)(vii)
Argument

The rejections are all submitted to be defective because the applied prior art does not teach or makes obvious the limitation of claims 1, 31 and 33, of a per anode or per cathode area agitation rate of 0.0001 to 10 liters per minute per cm^2 anode or cathode area", i.e. a normalized agitation rate of the basis of electrode area.

In other words, the determinative issue in each case (claims 1, 31, 33) is whether the prior art teaches per cathode or per anode area agitation rate to deposit nanocrystalline metallic material i.e. agitation rate normalized to electrode area (present in each of claims 1,31 and 33) and if not if this is the same as agitation rate/bath stirring without reference to the size of the electrode area.

The U.S.P.T.O has not pointed to any prior art which explicitly teaches per electrode area agitation rate but takes the position that this is the same as agitation rate without reference to anode or cathode area. On its face, this is wrong. In the case of the claims, the limitation is agitation rate divided by electrode area. In the U.S.P.T.O position, the "divided by" is ignored.

The action takes the position that " [a]gitation rate normalized to electrode area is considered to be a way of expressing amount of agitation" (page 4 of action) and "agitation rate normalized to electrode area is considered to pertain to amount of agitation" (page 6 of office action.) What is missing is any source cited to evidence a basis for the consideration (conclusion) that agitation rate normalized to electrode area expresses amount of agitation. Apparently the consideration (conclusion) is that of the Examiner and is therefore an ipse dixit and not a legitimate basis for rejection.

The rejection at page 8 says claim 1 "specifies the agitation rate based on the size of the cathode". This statement is overgeneralization.

What claims 1, 31 and 33 recite is a range for agitation rate per, i.e. divided by, area of anode or cathode, something very different from the general term "amount of agitation".

The rejection seems to imply the claims require a high rate of agitation. The application at page 5, lines 9-21 indicates differently: namely circulation rates over a wide range of conditions.

The action suggests that Lowenheim's or Gonzalez's or Biberbach's agitation meets the claims. If this is so, why don't any of these mention obtaining grain refinement (deposit of grain size less than 100nm). Why does not every plating process using Lowenheim's stirring, result in a grain size of <100nm? Why does Erb introduce pulsing to achieve grains sizes <100nm? According to the office action, shouldn't the stirring of Lowenheim" alone which Erb applies suffice to grain refine?

Applicant has pointed out that Lowenheim with high agitation has not stated he gets nanocrystalline structure. The U.S.P.T.O says maybe he does. This misses the point. If Lowenheim said he got nanocrystalline microstructure instead of being silent on this, this might be evidentiary support for the U.S.P.T.O.'s unsupported position.

Lowenheim rather applies stirring to prevent concentration and temperature gradients in the liquid electrolyte and not to control the microstructure of the deposit. Lowenheim's agitation deals with electrolyte uniformity and does not consider any implications of electrode size.

No support is given for the U.S.P.T.O. position on the technical issue as to whether per electrode area agitation rate is the same as general agitation rate,. i.e.,

stirring to remove concentration gradients in the electrolyte and expressed, e.g., in liters per minute. The U.S.P.T.O. says it doesn't need basis since the prior art agitation rate is obviously the same as the claim per electrode area agitation rate. But as indicated in the above, this is not correct.

Moreover, this is contrary to the overwhelming evidence relied on by applicant (detailed below) and present in the Evidence Appendix of this brief.

Firstly, there is Professor Erb's declaration of June 24, 2009 (Erb is an inventor in prior art used as a basis of rejection, namely U.S. Patent No. 5,433,797; copy present in Evidence Appendix submitted to the U.S.P.T.O. (on 07/01/2009) which states that the stirring of Erb (U.S. Patent No. 5,453,797 is a different property from and cannot be converted to agitation rate normalized to electrode rate without knowing the liters/minute provided by the stirring and the electrode areas and recitation thereof does not constitute a recognition that electrolyte flow, irrespective of electrolyte uniformity must be scaled to electrode size as a parameter for controlling microstructure grain size in an electrodeposit.

It is noted that the EPO, German Patent Office and Canadian Intellectual Property Offices all concluded that agitation rate normalized to electrode area is different from amount of agitation, i.e. the opposite of the ipse dixit "consideration" (ipse dixit conclusion) in the office action. See copy of EPO claims, Canadian Patent claims and translation of German Patent claims allowed in corresponding European, Canadian

and German patent applications (present in the Evidence Appendix hereto). Apparently, the Examiner here is the only one that has concluded that area normalized agitation rate is the same as amount of agitation. The rejections are clearly without scientific basis and are rebutted by evidence an d are therefore defective.

Note that claim 1 obtained in Germany (DE 10262102) is broader than present claim 34.

Note that claim 10 obtained in the EPO embraces claim 27 herein.

Note that claim 1 obtained in Canada and the claim obtained in the second Germany patent (DE10228323) embrace claim 28 herein.

37 C.F.R. 41.37(c)(1)(viii)

Appendix of claims involved in the appeal

1. Process for cathodically electrodepositing a selected metallic material on a permanent or temporary substrate in nanocrystalline form with an average grain size of less than 100 nm using electrodeposition at a deposition rate of at least 0.05 mm/h, comprising:

(a) providing an aqueous electrolyte containing ions of said metallic material, and

(b) agitating the electrolyte at a per anode or cathode area agitation rate of 0.0001 to 10 liter per min per cm^2 anode or cathode area.

2. Process as claimed in claim 27 or 28, characterized in that single or multiple D.C. cathodic-current pulses between said anode and said cathode are present and have a peak current density in the range of about 0.01 to 20 A/cm^2.

3. Process as claimed in claim 2, characterized in that the peak current density of the cathodic-current pulses is in the range of about 0.1 to 20 A/cm^2.

4. Process as claimed in claim 27 or 28, characterized in that said selected metallic material is (a) a pure metal or alloys of metals selected from the group consisting of Ag, Au, Cu, Co, Cr, Ni, Fe, Pb, Pd, Pt, Rh, Ru, Sn, V, W, Zn, or (b) an alloy

containing at least one of the elements of group (a) and alloying elements selected from the group consisting of C, P, S and Si.

5. Process as claimed in claim 27 or 28, characterized in that the t_{on}-time period is in the range of about 1 to about 50 msec, the t_{off}-time period is in the range of about 1 to 100 msec and the t_{anodic}-time period is in the range of about 1 to 10 msec.

6. Process as claimed in claim 27 or 28, characterized in that the duty cycle is in the range of 10 to 95 %.

7. Process as claimed in claim 27 or 28, characterized in that the cathodic-current pulse frequency ranges from 10 Hz to 350 Hz.

8. Process as claimed in Claim 1, characterized in that the deposition rate is at least 0.075 mm/h.

9. (canceled)

10. Process as claimed in claim 1, characterized by agitating the electrolyte by means of pumps, stirrers or ultrasonic agitation.

11. Process as claimed in claim 27 or 28, characterized by a relative motion between anode and cathode.

12. Process as claimed in claim 11, characterized in that the speed of the relative motion between anode and cathode ranges from 0 to 600 m/min.

13. Process as claimed in claim 11, characterized in that the relative motion is achieved by rotation of anode and cathode relative to each other.

14. Process as claimed in claim 13, characterized by a rotational speed of rotation of anode and cathode relative to each other ranging from 0.003 to 0.15 rpm.

15. Process as claimed in claim 11, characterized in that the relative motion is achieved by a mechanized motion generating a stroke of the anode and the cathode relative to each other.

16. Process as claimed in claim 11, characterized in that the anode is wrapped in an absorbent separator.

17. Process as claimed in claim 1, characterized in that said electrolyte contains a stress relieving agent or a grain refining agent selected from the group consisting of saccharin, coumarin, sodium lauryl sulfate and thiourea.

18. Process as claimed in Claim 1, characterized in that said electrolyte contains particulate additives in suspension selected from pure metal powders, metal

alloy powders or metal oxide powders of Al, Co, Cu, In, Mg, Ni, Si, Sn, V and Zn, nitrides of Al, B and Si, carbon C, carbides of B, Bi, Si, W, or organic materials, whereby the electrodeposited metallic material contains at least 5 % of said particulate additives.

19. Process as claimed in claim 18, characterized in that the electrodeposited metallic material contains at least 10 % of said particulate additives.

20. Process as claimed in claim 18, characterized in that the electrodeposited metallic material contains at least 20 % of said particulate additives.

21. Process as claimed in claim18, characterized in that the electrodeposited metallic material contains at least 30 % of said particulate additives.

22. Process as claimed in claim18, characterized in that said electro deposited metallic material contains at least 40 % of said particulate additives.

23. Process as claimed in claim 18, characterized in that the particulate additives average particle size is below 10 µm.

24. Micro component produced by an electrodeposition process as claimed in claim 1, having a maximum dimension of 1 mm, an average grain size equal to or smaller than 1000 nm, the ratio between the maximum dimension and the average grain size being greater than 10.

25. Micro component as claimed in claim 24, characterized in that the ratio between the maximum dimension of the micro component and the average grain size is greater than 100.

26. Micro component as claimed in claim 24, characterized by having an equiaxed micro structure.

27. Process according to Claim 1 characterized by:

(a) providing an anode and a cathode in contact with said electrolyte,

(b) passing single or multiple D.C. cathodic-current pulses between said anode and said cathode at a cathodic-current pulse frequency in a range of about 0 and 1000 Hz, at pulsed intervals during which said current passes for t_{on}-time period in the range of about 0.1 to 50 msec and does not pass for a t_{off}-time period in the range of about 0 to 500 msec,

(c) Passing single or multiple D.C. anodic-current pulses between said cathode and said anode at intervals during which said current passes for a t_{anodic}-time period in the range of 0 to 50 msec,

(d) a duty cycle being in a range of 5 to 100%; and

(e) a cathodic charge ($Q_{cathodic}$) per interval being always larger than a anodic charge (Q_{anodic}).

28. Process according to Claim 27, characterized by maintaining said electrolyte at a temperature in the range between 0 to 85°C.

29. Process as claimed in claim 4, characterized in that said selected metallic material is a pure metal selected from the group consisting of Co and Ni, containing P.

30. Process as claimed in claim 1, characterized in that said selected metallic material is an alloy of Fe with a pure metal selected from the group consisting of Co and Ni.

31. Process for cathodically electrodepositing a selected metallic material on a permanent or temporary substrate in nanocrystalline form with an average grain size of less than 100 nm at a deposition rate of at least 0.05 mm/h, comprising:

providing an aqueous electrolyte containing ions of said metallic material, agitating the electrolyte at a per anode or cathode area agitation rate in the range of 0.0001 to 10 liters per min per cm^2 anode or cathode area, and passing single or multiple cathode-current pulses between said anode and said cathode.

32. Micro component produced by a pulse electrodeposition process according to claim 31, having a maximum dimension of 1 mm, an average grain size equal to or smaller than 1000 nm, the ratio between the maximum dimension and the average grain size being greater than 10.

33. Process for cathodically electrodepositing a selected metallic material on a permanent or temporary substrate in nanocrystalline form with an average grain size of less than 100 nm at a deposition rate of at least 0.05 mm/h, comprising:

providing an aqueous electrolyte containing ions of said metallic material, agitating the electrolyte at a per anode or cathode area agitation rate in the range of 0.0001 to 10 liter per min per cm^2 anode or cathode area.

34. The process of claim 1 comprising passing single or multiple cathodic current pulses between said anode and said cathode.

37 C.F.R. 41.37(c)(1)(ix)
Evidence Appendix

The attached evidence is relied on herein.

The attached evidence consists of:

(1.) Declaration under 35 U.S.C. 1.132 of Uwe Erb of June 24, 2009, filed 7/1/09.

(2.) Copy of claims allowed in corresponding Canadian, EPO and German (English Translation) applications filed 9/29/09.

Evidence Appendix 1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of	)	
	)	
Gino PALUMBO, et al.	)	Group Art Unit: 1795
	)	
Patent Application No.: 10/516,300	)	Examiner: W. T. Leader
	)	
Filed: December 9, 2004	)	Confirmation No.: 5590
	)	
For: PROCESS FOR ELECTROPLATING METALLIC AND METALL MATRIX COMPOSITE FOILS, COATINGS AND MICROCOMPONENTS	)	Attorney Dkt No.: BROO3001/ESS

DECLARATION UNDER 35 U.S.C. 1§132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

UWE Erb hereby declares:

1. I am currently a Professor of Materials Science and Engineering in the Faculty of Applied Science at the University of Toronto.

2. The focus of my research since the early 1980's is in the areas of Interface Control in Materials and Nanostructured Materials.

3. My research team is internationally recognized as the leading group in the world in the development of electrochemical synthesis methods of nanostructured metals, alloys and composites. These materials have outstanding physical, chemical and mechanical properties usually not observed in conventional materials. Applications include wear and corrosion resistant coatings, environmentally benign replacement coatings for chromium and cadmium, nuclear steam generator repair, soft ferromagnetic materials for high performance motors and power supplies, and high strength structural materials for automotive, aerospace and consumer products.
4. I am the named inventor of several patents including U.S. Patent No. 5,433,797 and U.S. Patent No. 5,353,266; which were the first patents in the world dealing with nanomaterials made by an electrodeposition process.
5. I am also co-author of close to 200 scientific and technical papers in the field of producing nanomaterials using electrodeposition, published in international, leading journals and conference proceedings.
6. I am a scientific advisor for and a shareholder in Integran Technologies, Inc.
7. I understand that my patent (U.S. Patent No. 5,433,797) has been applied by the U.S. Patent and Trademark Office to reject claims in the U.S. Patent Application No. 10/516,300. My patent does not mention mixing or agitation. Example 7 of my patent says continuous stirring (0-500rpm) may be present. The purpose of this stirring in Example 7 was to remove concentration gradients and temperature gradients in the electroplating bath. The purpose of the stirring in Example 7 was

not to control microstructure grain size of an electrodeposit so it is nanocrystalline.

8. The continuous stirring mentioned in Example 7 is a different property from agitation rate normalized to electrode area and cannot be converted thereto without knowing the liters/minute provided by the stirring and the electrode areas and recitation thereof does not constitute a recognition that electrolyte flow, irrespective of electrolyte uniformity must be scaled to electrode size as a parameter for controlling microstructure grain size in an electrodeposit.
9. Declarant acknowledges that all willful false statements and the like are punishable by a fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statement may jeopardize the validity of this application or any patent issuing thereon.

June 24, 2009
Date

Uwe Erb

Brevet canadien / Canadian Patent

Le commissaire aux brevets a reçu une demande de délivrance de brevet visant une invention. Ladite requête satisfait aux exigences de la *Loi sur les brevets*. Le titre et la description de l'invention figurent dans le mémoire descriptif, dont une copie fait partie intégrante du présent document.

Le présent brevet confère à son titulaire et à ses représentants légaux, pour une période expirant vingt ans à compter de la date du dépôt de la demande au Canada, le droit, la faculté et le privilège exclusif de fabriquer, construire, exploiter et vendre à d'autres, pour qu'ils l'exploitent, l'objet de l'invention, sauf jugement en l'espèce rendu par un tribunal compétent, et sous réserve du paiement des taxes périodiques.

The Commissioner of Patents has received a petition for the grant of a patent for an invention. The requirements of the *Patent Act* have been complied with. The title and a description of the invention are contained in the specification, a copy of which forms an integral part of this document.

The present patent grants to its owner and to the legal representatives of its owner, for a term which expires twenty years from the filing date of the application in Canada, the exclusive right, privilege and liberty of making, constructing and using the invention and selling it to others to be used, subject to adjudication before any court of competent jurisdiction, and subject to the payment of maintenance fees.

BREVET CANADIEN	**2,490,464**	CANADIAN PATENT
Date à laquelle le brevet a été accordé et délivré	**2008/09/02**	Date on which the patent was granted and issued
Date du dépôt de la demande	**2002/06/25**	Filing date of the application
Date à laquelle la demande est devenue accessible au public pour consultation	**2003/12/31**	Date on which the application was made available for public inspection

Commissaire aux brevets / Commissioner of Patents

Canada

Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

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CANADIAN PATENT

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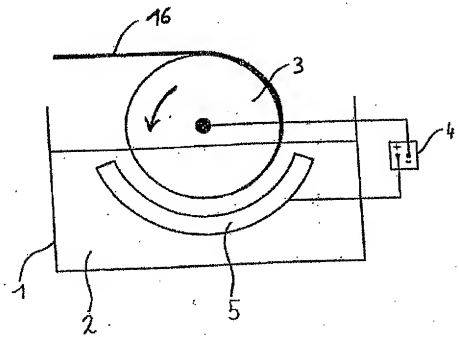
(74) Agent: RIDOUT & MAYBEE LLP

(54) Titre : PROCEDE DE PLAQAGE ELECTROCHIMIQUE DE FEUILLES METALLIQUES ET DE COMPOSITES A MATRICE METALLIQUE, DE REVETEMENTS ET DE MICROCOMPOSANTS

(54) Title: PROCESS FOR ELECTROPLATING METALLIC AND METALL MATRIX COMPOSITE FOILS, COATINGS AND MICROCOMPONENTS



(57) Abrégé/Abstract:
The invention relates to a process for forming coatings or free-standing deposits of nano-crystalline metals, metal alloys or metal matrix composites. The process employs drum plating or selective plating processes involving pulse electrode-position and a non-stationary anode or cathode. Novel nano-crystalline metal matrix composites and micro components are disclosed as well. Also described is a process for forming micro-components with grain sizes below 1,000nm.

CLAIMS

1. Process for cathodically electrodepositing a selected metallic material on a permanent or temporary substrate in nanocrystalline form with an average grain size of less than 100 nm at a deposition rate of at least 0.05 mm/h, comprising:

providing an aqueous electrolyte containing ions of said metallic material,

maintaining said electrolyte at a temperature in the range between 0 to 85°C,

agitating the electrolyte at an agitation rate in the range of 0.0001 to 10 litre per min and per cm^2 anode or cathode area or at an agitation rate in the range of 1 to 750 millilitre per mm and per Ampere,

providing an anode and a cathode in contact with said electrolyte, passing single or multiple D.C. cathodic-current pulses between said anode and said cathode, at intervals during which said current passes for a $t_{cathodic\text{-}on}$-time period is in the range of 0.1 to 50 msec and does not pass for a $t_{cathodic\text{-}off}$-time period is in the range of 0 to 500 msec, and passing single or multiple D.C. anodic-current pulses between said cathode and said anode at intervals during which said current passes for a $t_{anodic\text{-}on}$-time period is in the range of 0 to 50 msec, a duty cycle being in a range of 5 to 100% and a cathodic charge ($Q_{cathodic}$) per interval being always larger than a anodic charge (Q_{anodic}).

Evidence Appendix 7

2 Process according to claim 1, wherein the single or multiple D.C. cathodic-current pulses between said anode and said cathode have a peak current density in the range of 0.01 to 20 A/cm^2.

3. Process according to claim 2, wherein the peak current density of the cathodic-current pulses is in the range of 0.1 to 20 A/cm^2.

4. Process according to claim 3, wherein the peak current density of the cathodic-current pulses is in the range of 1 to 10 A/cm^2.

5. Process according to any one of claims 1 to 4, wherein said selected metallic material is (a) a pure metal selected from the group consisting of Ag, Au, Cu, Co, Cr, Ni, Fe, Pb, Pd, Rt, Rh, Ru, Sn, V, W, Zn, or (b) an alloy containing at least one of the elements of group (a) and alloying elements selected from the group consisting of C, P, S and Si.

6. Process according to any one of claims 1 to 5, wherein the duty cycle is in the range of 10 to 95 %.

7. Process according to claim 6, wherein the duty cycle is in the range of 20 to 80%.

8. Process according to any one of claims 1 to 7, wherein the deposition rate is at least 0.075 mm/h.

9. Process according to claim 8, wherein the deposition rate is at least 0.1 mm/h.

Evidence Appendix 8

29. Micro component having a maximum dimension of 1 mm produced by the electrodeposition process according to any one of claims 1 to 28, wherein the nanocrystalline metallic material has an average grain size less than 100 nm, the ratio between the maximum dimension and the average grain size being greater than 10.

30. Micro component according to claim 29, wherein the ratio between the maximum dimension of the micro component and the average grain size is greater than 100.

31. Micro component according to any one of claims 29 to 30, which has an equiaxed microstructure.

Europe

Evidence Appendix 9

URKUNDE	CERTIFICATE	CERTIFICAT
Es wird hiermit bescheinigt, dass für die in der Patentschrift beschriebene Erfindung ein europäisches Patent für die in der Patentschrift bezeichneten Vertragsstaaten erteilt worden ist.	It is hereby certified that a European patent has been granted in respect of the invention described in the patent specification for the Contracting States designated in the specification.	Il est certifié qu'un brevet européen a été délivré pour l'invention décrite dans le fascicule de brevet, pour les Etats contractants désignés dans le fascicule de brevet.

Europäisches Patent Nr.	European patent No.	Brevet européen n°
	1516076	
Patentinhaber	Proprietor of the patent	Titulaire du brevet

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President of the European Patent Office
Présidente de l'Office européen des brevets

München, den
Munich,
Fait à Munich, le 27.02.08

EPA/EPO/OEB 2001 0207

(19) Europäisches Patentamt
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(12) EUROPEAN PATENT SPECIFICATION

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C25D 15/02 (2006.01)

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(54) PROCESS FOR ELECTROPLATING METALLIC AND METALL MATRIX COMPOSITE FOILS, COATINGS AND MICROCOMPONENTS

VERFAHREN ZUR ELEKTROPLATTIERUNG VON METALLISCHEN UND METALL-MATRIX-COMPOSITE FOLIEN, BESCHICHTUNGEN UND MIKROKOMPONENTEN

PROCEDE DE PLACAGE ELECTROCHIMIQUE DE FEUILLES METALLIQUES ET DE COMPOSITES A MATRICE METALLIQUE, DE REVETEMENTS ET DE MICROCOMPOSANTS

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EP 1 516 076 B1

Electrolyte circulation rate: None
Electrolyte Formulation:

300 g/l $NiSO_4 \cdot 7H_2O$
45 g/l $NiCl_2 \cdot 6H_2O$
45 g/l H_3BO_3
2 g/l Sodium Saccharinate
3 ml/l NPA-91
pH 3.0

Average grain size: 15-20nm
Hardness: 600Vickers

[0057] The nano-fingers exhibited a significantly higher contact force when compared to "conventional grain-sized" fingers.

Claims

1. Process for cathodically electrodepositing a selected metallic material on a permanent or temporary substrate in nanocrystalline form with an average grain size of less than 100 nm using pulse electrodeposition at a deposition rate of at least 0.05 mm/h, comprising:

providing an aqueous electrolyte containing ions of said metallic material, maintaining said electrolyte at a temperature in the range between 0 to 65°C, providing an anode and a cathode in contact with said electrolyte, passing single or multiple D.C. cathodic-current pulses between said anode and said cathode at a cathodic-current pulse frequency in a range of about 0 and 1000 Hz, at pulsed intervals during which said current passes for a t_{on}-time period in the range of about 0.1 to 50 msec and does not pass for a t_{off}-time period in the range of about 0 to 500 msec, and passing single or multiple D.C. anodic-current pulses between said cathode and said anode at intervals during which said current passes for a t_{anodic}-time period in the range of 0 to 50 msec, a duty cycle being in a range of 5 to 100% and a cathodic charge ($Q_{cathodic}$) per interval being always larger than a anodic charge (Q_{anodic}).

2. Process as claimed in claim 1, **characterized in that** the single or multiple D.C. cathodic-current pulses between said anode and said cathode have a peak current density in the range of about 0.01 to 20 A/cm².

3. Process as claimed in claim 2, **characterized in that** the peak current density of the cathodic-current pulses is in the range of about 0.1 to 20 A/cm², preferably in the range of about 1 to 10 A/cm².

4. Process as claimed in any of claims 1 to 3, **characterized in that** said selected metallic material is (a) a pure metal selected from the group consisting of Ag, Au, Cu, Co, Cr, Ni, Fe, Pb, Pd, Rt, Rh, Ru, Sn, V, W, Zn, or (b) an alloy containing at least one of the elements of group (a) and alloying elements selected from the group consisting of C, P, S and Si.

5. Process as claimed in any of claims 1 to 4, **characterized in that** the t_{on}-time period is in the range of about 1 to about 50 msec, the t_{off}-time period is in the range of about 1 to 100 msec and the t_{anodic}-time period is in the range of about 1 to 10 msec.

6. Process as claimed in any of claims 1 to 5, **characterized in that** the duty cycle preferably is in the range of 10 to 95 %, and more preferably is in the range of 20 to 80 %.

7. Process as claimed in any of claims 1 to 6, **characterized in that** the cathodic-current pulse frequency ranges from 10 Hz to 350 Hz.

8. Process as claimed in any of claims 1 to 7, **characterized in that** the deposition rate is preferably at least 0.075 mm/h and more preferably at least 0.1 mm/h.

9. Process as claimed in any of claims 1 to 8, **characterized by** agitating the electrolyte at an agitation rate in the

range of 0 to 750 ml/(min.xA), preferably in a range of 0 to 500 ml/(min.xA).

10. Process as claimed in any of claims 1 to 8, characterized by agitating the electrolyte at an agitation rate in the range of 0,0001 to 10 l/(min.xcm ^{2}) (liter per min per cm^2 anode or cathode area).

11. Process as claimed in claim 9 or 10, characterized by agitating the electrolyte by means of pumps, stirrers or ultrasonic agitation.

12. Process as claimed in any of claims 1 to 11, characterized by a relative motion between anode and cathode.

13. Process as claimed in claim 12, characterized in that the speed of the relative motion between anode and cathode ranges from 0 to 600 m/min, preferably from 0.003 to 10 m/min.

14. Process as claimed in claim 12, characterized in that the relative motion is achieved by rotation of anode and cathode relative to each other.

15. Process as claimed in claim 14, characterized by a rotational speed of rotation of anode and cathode relative to each other ranging from 0.003 to 0.15 rpm and preferably from 0.003 to 0.05 rpm.

16. Process as claimed in claim 12 or claim 13, characterized in that the relative motion is achieved by a mechanized motion generating a stroke of the anode and the cathode relative to each other.

17. Process as claimed in claim 12 or 16, characterized in that the anode is wrapped in an absorbent separator.

18. Process as claimed in any of claims 1 to 17, characterized in that said electrolyte contains a stress relieving agent or a grain refining agent selected from the group of saccharin, coumarin, sodium lauryl sulfate and thiourea.

19. Process as claimed in any of claims 1 to 18, characterized in that said electrolyte contains particulate additives in suspension selected from pure metal powders, metal alloy powders or metal oxide powders of Al, Co, Cu, In, Mg, Ni, Si, Sn, V and Zn, nitrides of Al, B and Si, carbon C (graphite or diamond), carbides of B, Bi, Si, W, or organic materials such as PTFE and polymers spheres, whereby the electrodeposited metallic material contains at least 5 % of said particulate additives.

20. Process as claimed in claim 19, characterized in that the electrodeposited metallic material contains at least 10 % of said particulate additives.

21. Process as claimed in claim 19, characterized in that the electrodeposited metallic material contains at least 20 % of said particulate additives.

22. Process as claimed in claim9, characterized in that the electrodeposited metallic material contains at least 30 % of said particulate additives.

23. Process as claimed in claim9, characterized in that said electro deposited metallic material contains at least 40 % of said particulate additives.

24. Process as claimed in any of claims 19 to 23, characterized in that the particulate additives average particle size is below 10 µm, preferably below 1000 nm, more preferably below 500 nm and most preferably below 100 nm.

25. Micro component produced by a pulse electrodeposition process as claimed in any of claims 1 to 23, having a maximum dimension of 1 mm, an average grain size less than 100 nm, the ratio between the maximum dimension and the average grain size being greater than 10.

26. Micro component as claimed in claim 25, characterized in that the ratio between the maximum dimension of the micro component and the average grain size is greater than 100.

27. Micro component as claimed in claim 25 or 26, characterized by having a equiaxed micro structure.

Patentansprüche

1. Verfahren zum kathodischen Elektroabscheiden eines ausgewählten metallischen Materials auf einem dauerhaften oder zeitweisen Substrat in nanokristalliner Form mit einer Durchschnittskorngröße von weniger als 100 nm, unter Verwendung von Puls-Elektroabscheidan, mit einer Abscheidungsgeschwindigkeit von wenigstens 0,05 mm/h, aufweisend:

Vorsehen eines wässrigen Elektrolyts, welcher Ionen desmetallischen Materials enthält, Halten des Elektrolyten bei einer Temperatur im Bereich zwischen 0 bis 85° C, Vorsehen einer Anode und einer Kathode in Kontakt mit dem Elektrolyt, Durchleiten von einzelnen oder mehreren Gleichstromkathodenstrompulsen zwischen der Anode und Kathode mit einer Kathodenstrompulsfrequenz in einem Bereich zwischen 0 und 1000 Hz zu gepulsten Intervallen, während denen der Strom für eine t_{on}-Zeitperiode im Bereich von ungefähr 0,1 bis 50 ms fließt und für eine t_{off}-Zeitperiode im Bereich von 0 bis 500 ms nicht fließt, und Durchleiten von einzelnen oder mehreren Gleichstromanodenstrompulsen zwischen der Kathode und Anode zu intervallen, während denen der Strom für einer $t_{anodisch}$-Zeitperiode im Bereich von 0 bis 50 ms fließt, wobei ein Arbeitszyklus im Bereich von 5 bis 100% ist und eine kathodische Ladung ($Q_{kathodisch}$) pro Intervall immer größer als eine anodische Ladung ($Q_{anodisch}$) ist.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die einzelnen oder mehreren Gleichstrom-Kathodenstromimpulse zwischen der Anode und der Kathode eine Spitzenstromdichte im Bereich von etwa 0,01 bis 20 A/cm² aufweisen.

3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, dass die Spitzenstromdichte der Kathodenstrompulse im Bereich von etwa 0,1 bis 20 A/cm², bevorzugt im Bereich von 1 bis 10 A/cm² liegt.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, dass das ausgewählte metallische Material (a) ein reines Metall ist, ausgewählt aus der Gruppe bestehend aus Ag, Au, Cu, Co, Cr, Ni, Fe, Pb, Pd, Rt, Rh, Ru, Sn, V, W, Zn oder (b) eine Legierung, bestehend aus zumindest einem der Elemente der Gruppe (a) und legierenden Elementen, ausgewählt aus der Gruppe bestehend aus C, P, S und Si.

5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, dass die t_{on}-Zeitperiode im Bereich von 1 bis etwa 50 ms liegt, die t_{aus}-Zeitperiode im Bereich von etwa 1 bis 100 ms und die $t_{anodisch}$-Zeitperiode im Bereich von etwa 1 bis 10 ms liegt.

6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, dass der Arbeitszyklus bevorzugt im Bereich von 10 bis 95% liegt, und bevorzugter im Bereich von 20 bis 80% liegt.

7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, dass die Kathodenstrom-Pulsfrequenz von 10 Hz bis 350 Hz reicht.

8. Verfahren nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, dass die Abscheidungsgeschwindigkeit bevorzugt zumindest 0,075 mm/h und bevorzugter zumindest 0,1 mm/h ist.

9. Verfahren nach einem der Ansprüche 1 bis 8, gekennzeichnet durch Umrühren des Elektrolyten bei einer Umrührgeschwindigkeit im Bereich von 0 bis 750 ml/min/A, bevorzugt im Bereich von 1 bis 500 ml/min/A.

10. Verfahren nach einem der Ansprüche 1 bis 8, gekennzeichnet durch Umrühren des Elektrolyten bei einer Umrührgeschwindigkeit im Bereich von 0,0001 bis 10 l/min/cm² (Liter pro Minute perom² Anoden- oder Kathodenfläche).

11. Verfahren nach Anspruch 9 oder 10, gekennzeichnet durch Umrühren des Elektrolyten mittels Pumpen, Rührwerken oder Ultraschallanregung.

12. Verfahren nach einem der Ansprüche 1 bis 11, gekennzeichnet durch eine relative Bewegung zwischen der Anode und Kathode.

13. Verfahren nach Anspruch 12, dadurch gekennzeichnet, dass die Geschwindigkeit der relativen Bewegung zwischen Anode und Kathode von 0 bis zu 600 m/min reicht, bevorzugt von 0,003 bis 10 m/min.

14. Verfahren nach Anspruch 12, **dadurch gekennzeichnet, dass** die relative Bewegung durch Drehung der Anode und der Kathode relativ zueinander erreicht wird.

15. Verfahren nach Anspruch 14, **gekennzeichnet durch eine** Rotationsgeschwindigkeit der Rotation der Anode und der Kathode relativ zueinander, welche von 0,003 bis 0,15 Upm und bevorzugt von 0,003 bis 0,05 Upm reicht.

16. Verfahren nach Anspruch 12 oder 13, **dadurch gekennzeichnet, dass die** relative Bewegung durch einen eine mechanisierte Bewegung erzeugenden Hub der Anode und der Kathode relativ zueinander erreicht wird.

17. Verfahren nach Anspruch 12 oder 16, **dadurch gekennzeichnet, dass** die Anode in ein absorbierendes Abstandstück gewickelt ist.

18. Verfahren nach irgendeinem der Ansprüche 1 bis 17, **dadurch gekennzeichnet, dass** der Elektrolyt ein spannungssenkendes Mittel oder ein Konverfeinerungsmittel enthält, ausgewählt aus der Gruppe von Saccharin, Cumarin, Natriumlaurylsulfat und Thio-Harnstoff.

19. Verfahren nach irgendeinem der Ansprüche 1 bis 18, **dadurch gekennzeichnet, dass** der Elektrolyt aus Partikeln bestehende Zusätze in der Lösung enthält, ausgewählt aus reinen Metallpulvern, Metalllegierungspulvern oder Metalloxidpulvern von Al, Co, Cu, In, Mg, Ni, Si, Sn, V und Zn, Nitriden von Al, B und Si, Kohlenstoff C (Graphit oder Diament), Carbide von B, Bi, Si, W oder organische Materialien wie PTFE und Polymerkugeln, wobei das elektro-abgeschiedene metallische Material zumindest 5% der aus Partikeln bestehenden Zusätze enthält.

20. Verfahren nach Anspruch 19, **dadurch gekennzeichnet, dass** das elektro-abgeschiedene metallische Material zumindest 10% der aus Partikeln bestehenden Zusätze enthält.

21. Verfahren nach Anspruch 19, **dadurch gekennzeichnet, dass** das elektro-abgeschiedene metallische Material zumindest 20% der aus Partikeln bestehenden Zusätze enthält.

22. Verfahren nach Anspruch 19, **dadurch gekennzeichnet, dass** das elektro-abgeschiedene metallische Material zumindest 30% der aus Partikeln bestehenden Zusätze enthält.

23. Verfahren nach Anspruch 19, **dadurch gekennzeichnet, dass** das elektro-abgeschiedene metallische Material zumindest 40% der aus Partikeln bestehenden Zusätze enthält.

24. Verfahren nach irgendeinem der Ansprüche 19 bis 23, **dadurch gekennzeichnet, dass** die durchschnittliche Partikelgröße der aus Partikeln bestehenden Zusätze unter 10 µm liegt, bevorzugt unter 1000 nm, bevorzugter unter 500 nm, und am bevorzugtesten unter 100 nm.

25. Mikrokomponente, hergestellt durch ein Pulselektroabscheidungsverfahren wie in einem der Ansprüche 1 bis 23 beansprucht, welche eine maximale Abmessung von 1 mm aufweist, eine Durchschnittskorngröße kleiner 100 nm, wobei das Verhältnis zwischen der maximalen Abmessung und der Durchschnittskorngröße größer als 10 ist.

26. Mikrokomponente nach Anspruch 25, **dadurch gekennzeichnet, dass** das Verhältnis zwischen der maximalen Abmessung der Mikrokomponente und der Durchschnittskorngröße größer als 100 ist.

27. Mikrokomponente nach Anspruch 25 oder 26, **gekennzeichnet dadurch, dass** sie eine gleichachsige Mikrostruktur aufweist.

Revendications

1. Procédé d'électrodéposition par voie cathodique d'un matériau métallique choisi sur un substrat permanent ou temporaire sous une forme nanocristalline avec une dimension de grain moyenne inférieure à 100 nm en utilisant une électrodéposition à impulsions à un débit de dépôt d'au moins 0,05 mm/h, comprenant :

   la fourniture d'un électrolyte aqueux renfermant des ions dudit matériau métallique, le maintien dudit électrolyte à une température comprise dans la gamme entre 0 et 85°C, la fourniture d'une anode et d'une cathode en contact avec ledit électrolyte, le passage d'impulsions de courant cathodique de courant continu simples ou

multiples entre ladite anode et ladite cathode à une fréquence d'impulsions de courant cathodique dans la gamme d'environ 0 à 1000 Hz, à des intervalles puisés au cours desquels ledit courant passe pendant une période de temps t_{act} dans la gamme d'environ 0,1 à 50 ms et ne passe pas pendant une période de temps $t_{désact}$ dans la gamme d'environ 0 à 500 ms et le passage d'impulsions de courant anodique de courant continu simples ou multiples entre ladite cathode et ladite anode à des intervalles pendant lesquels ledit courant passe pendant une période de temps $t_{anodique}$ dans la gamme de 0 à 50 ms, un cycle de service dans la gamme de 5 à 100 % et une charge cathodique ($C_{cathodique}$) par intervalle qui est toujours supérieure à une charge anodique ($C_{anodique}$).

2. Procédé selon la revendication 1, **caractérisé en ce que** les impulsions de courant cathodique de courant continu simples ou multiples entre ladite anode et ladite cathode ont une densité de courant de pic dans la gamme d'environ 0,01 à 20 A/cm².

3. Procédé selon la revendication 2, **caractérisé en ce que** la densité de courant de pic des impulsions de courant cathodique se situe dans la gamme d'environ 0,1 à 20 A/cm², de préférence dans la gamme d'environ 1 à 10 A/cm².

4. Procédé selon l'une quelconque des revendications 1 à 3, **caractérisé en ce que** ledit matériau métallique choisi est (a) un métal pur choisi parmi le groupe comprenant Ag, Au, Cu, Co, Cr, Ni, Fe, Pb, Pd, Pt, Rh, Ru, Sn, Y, W, Zn ou (b) un alliage renfermant au moins un des éléments du groupe (a) et des éléments d'alliage choisis dans le groupe comprenant C, P, S et Si.

5. Procédé selon l'une quelconque des revendications 1 à 4, **caractérisé en ce que** la période de temps t_{act} se situe dans la gamme d'environ 1 à environ 50 ms, la période de temps $t_{désact}$ se situe dans la gamme d'environ 1 à 100 ms et la période de temps $t_{anodique}$ se situe dans la gamme d'environ 1 à 10 ms.

6. Procédé selon l'une quelconque des revendications 1 à 5, **caractérisé en ce que** le cycle de service se situe, de préférence, dans la gamme de 10 à 95 % et mieux encore se situe dans la gamme de 20 à 80 %.

7. Procédé selon l'une quelconque des revendications 1 à 6, **caractérisé en ce que** la fréquence d'impulsions de courant cathodique se situe de 10 Hz à 350 Hz.

8. Procédé selon l'une quelconque des revendications 1 à 7, **caractérisé en ce que** la vitesse de dépôt est, de préférence, d'au moins 0,075 mm/h et mieux encore d'au moins 0,1 mm/h.

9. Procédé selon l'une quelconque des revendications 1 à 8, **caractérisé par** l'agitation de l'électrolyte à une vitesse d'agitation dans la gamme de 0 à 750 ml/(min x A), de préférence dans une gamme de 0 à 500 ml/(min x A).

10. Procédé selon l'une quelconque des revendications 1 à 8, **caractérisé par** l'agitation de l'électrolyte à une vitesse d'agitation dans la gamme de 0,0001 à 10 l/(min x cm²) (litre par min par cm² de surface d'anode ou de cathode).

11. Procédé selon la revendication 9 ou 10, **caractérisé par** l'agitation de l'électrolyte au moyen de pompes, d'agitateurs ou une agitation par ultrasons.

12. Procédé selon l'une quelconque des revendications 1 à 11, **caractérisé par** un mouvement relatif entre l'anode et la cathode.

13. Procédé selon la revendication 12, **caractérisé en ce que** la vitesse du mouvement relatif entre l'anode et la cathode se situe de 0 à 600 m/min, de préférence de 0,003 à 10 m/min.

14. Procédé selon la revendication 12, **caractérisé en ce que** le mouvement relatif est obtenu par rotation de l'anode et de la cathode relativement l'une à l'autre.

15. Procédé selon la revendication 14, **caractérisé par** une vitesse de rotation de l'anode et de la cathode relativement l'une à l'autre dans la gamme de 0,03 à 0,15 tour par minute et, de préférence, de 0,003 à 0,05 tour par minute.

16. Procédé selon la revendication 12 ou la revendication 13, **caractérisé en ce que** le mouvement relatif est obtenu par un mouvement mécanisé générant une course de l'anode et de la cathode relativement l'une à l'autre.

17. Procédé selon la revendication 12 ou 16, **caractérisé en ce que** l'anode est enveloppée dans un séparateur absorbant.

18. Procédé selon l'une quelconque des revendications 1 à 17, **caractérisé en ce que** ledit électrolyte renferme un agent de libération de contrainte ou un agent de raffinage de grain choisi dans le groupe de la saccharine, de la coumarine, du lauryl sulfate de sodium et de la thiourée.

19. Procédé selon l'une quelconque des revendications 1 à 18, **caractérisé en ce que** ledit électrolyte renferme des additifs particulaires en suspension choisis parmi les poudres de métal pur, les poudres d'alliage de métal et les poudres d'oxydes métalliques de Al, Co, Cu, In, Mg, Ni, Si, Sn, V et Zn, les nitrures de Al, B et Si, le carbone C (graphite ou diamant), les carbures de B, Bi, Si, W ou des matériaux organiques comme PTFE et des sphères de polymères, de sorte que le matériau métallique électrodéposé renferme au moins 5 % desdits additifs particulaires.

20. Procédé selon la revendication 19, **caractérisé en ce que** le matériau métallique électrodéposé renferme au moins 10 % desdits additifs particulaires.

21. Procédé selon la revendication 19, **caractérisé en ce que** le matériau métallique électrodéposé renferme au moins 20 % desdits additifs particulaires.

22. Procédé selon la revendication 19, **caractérisé en ce que** le matériau métallique électrodéposé renferme au moins 30 % desdits additifs particulaires.

23. Procédé selon la revendication 19, **caractérisé en ce que** ledit matériau métallique électrodéposé renferme au moins 40 % desdits additifs particulaires.

24. Procédé selon l'une quelconque des revendications 19 à 23, **caractérisé en ce que** la dimension de particule moyenne des additifs particulaires est inférieure à 10 µm, de préférence inférieure à 1000 nm, plus particulièrement inférieure à 500 nm et mieux encore inférieure à 100 nm.

25. Microcomposant produit par un procédé d'électrodéposition à impulsions selon l'une quelconque des revendications 1 à 23, ayant une dimension maximum de 1 mm, une dimension de grain moyenne inférieure à 100 nm, le rapport entre la dimension maximum et la dimension de grain moyenne étant supérieur à 10.

26. Microcomposant selon la revendication 25, **caractérisé en ce que** le rapport entre la dimension maximum du microcomposant et la dimension de grain moyenne est supérieur à 100.

27. Microcomposant selon la revendication 25 ou 26, **caractérisé en ce qu'il** présente une microstructure équiaxiale.

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Integran Technologies Inc.

Claims

1. Process for cathodically electrodepositing a selected metallic material on a permanent or temporary substrate in nanocrystalline form with an average grain size of less than 100 nm at a deposition rate of at least 0.05 mm/h, comprising:
providing an aqueous electrolyte containing ions of said metallic material,
agitating the electrolyte at an agitation rate in the range of 0.0001 to 10 liter per min and per cm^2 anode or cathode area or at an agitation rate in the range of 1 to 750 milliliter per min and per Ampere, and
passing single or multiple cathodic-current pulses between said anode and said cathode.

2. Process according to claim 1, wherein a duty cycle is in a range of 5 to 100%.

3. Process according to any of claims 1 to 2, wherein a frequency of the cathodic-current pulses is in a range of 0 to 1000 Hz.

4. Process according to any of claims 1 to 3, wherein the single or multiple cathodic-current pulses between said anode and said cathode have a peak current density in the range of about 0.01 to 20 A/cm^2.

5. Process according to claim 4, wherein the peak current density of the cathodic-current pulses is in the range of 0.1 to 20 A/cm^2 preferably in the range of 1 to 10 A/cm^2.

6. Process according to any of claims 1 to 5, wherein said selected metallic material is (a) a pure metal selected from the group consisting of Ag, Au, Cu, Co, Cr, Ni, Fe, Pb, Pd, Rt, Rh, Ru, Sn, V, W, Zn, or (b) an alloy containing at least one of the elements of group (a) and alloying elements selected from the group consisting of C, P, S and Si.

7. Process according to any of claims 1 to 6, wherein a $t_{cathodic\text{-}on}$-time period is in the range of 0.1 to 50 msec, a $t_{cathodic\text{-}off}$-time period is in the range of 0 to 500 msec and a $t_{anodic\text{-}on}$-time period is in the range of 0 to 50 msec.

8. Process according to any of claims 2 to 7, wherein the duty cycle is in the range of 10 to 95 %.

9. Process according to any of claims 1 to 8, wherein the deposition rate is at least 0.075 mm/h and preferably at least 0.1 mm/h.

10. Process according to any of claims 1 to 9, which comprises agitating the electrolyte at an agitation rate in the range of 1 to 500 milliliter per min and per Ampere.

11. Process according to any of claims 1 to 10, which comprises agitating the electrolyte by means of pumps, stirrers or ultrasonic agitation.

12. Process according to any of claims 1 to 10, which comprises a relative motion between anode and cathode.

13. Process according to claim 12, wherein the speed of the relative motion between anode and cathode ranges from 0 to 600 m/min, preferably in the range from 0.003 to 10 m/min.

14. Process according to any of claims 12, wherein the relative motion is achieved by rotation of anode and cathode relative to each other.

15. Process according to claim 14, wherein a rotational speed of rotation of anode and cathode relative to each other ranges from 0.003 to 0.15 rpm and preferably between 0.003 to 0.05 rpm.

16. Process according to claim 12 to 13, wherein the relative motion is achieved by a mechanized motion generating a stroke of the anode and the cathode relative to each other.

17. Process according to claim 12 or 16, wherein the anode is wrapped in an absorbent separator.

18. Process according to any of claims 1 to 17, wherein said electrolyte contains a stress relieving agent or a grain refining agent selected from the group of saccharin, coumarin, sodium lauryl sulfate and thiourea.

19. Process according to any of claims 1 to 18, wherein said electrolyte contains particulate additives in suspension selected from pure metal powders, metal alloy powders or metal oxide powders of Al, Co, Cu, In, Ng, Ni, Si, Sn, V and Zn, nitrides of Al, B and Si, carbon C (graphite or diamond), carbides of B, Bi, Si, W, or organic materials such as PTFE and polymers spheres, whereby the electrodeposited metallic material contains at least 5 % of said particulate additives.

20. Process according to claim 19, wherein the electrodeposited metallic material contains at least 10 % of said particulate additives.

21. Process according to claim 19, wherein the electrodeposited metallic material contains at least 20 % of said particulate additives.

22. Process according to claim 19, wherein the electrodeposited metallic material contains at least 30 % of said particulate additives.

23. Process according to claim 19, wherein said electro deposited metallic material contains at least 40 % of said particulate additives.

24. Process according to any of claims 19 to 23, wherein the particulate additives average particle size is below 10 µm preferably below 1000 nm, preferably below 500 nm, preferably below 100 nm and most preferably below 100 nm

Conclusion

Thus, what is the case is that the U.S.P.T.O position is supported by no evidence, Applicant's position is supported by overwhelming evidence.

The rejections are blatantly defective.

Reversal of the Rejection is Required

The undersigned submitted a pre-appeal brief request for review to give to the U.S.P.T.O a chance to correct the shortcomings of the rejections. In response, reopening of prosecution was refused. The implication is that shortcomings of the rejection cannot be corrected. Therefore, reopening prosecution at this point should not be an option and reversal of the rejection and allowance should rather be what is implemented.

Fees

The $540.00 fee required by 37 C.F. R. 41.37 (b) and 37 C.F. R. 41.20 (b) (2) is authorized to be charged to deposit account number 02-0200.

Respectfully submitted,
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